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**Title:** Structure and magnetic properties of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics prepared by sintering, mechanical activation and EDAMM process. A comparative study

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## STRUCTURE AND MAGNETIC PROPERTIES OF $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ CERAMICS PREPARED BY SINTERING, MECHANICAL ACTIVATION AND EDAMM PROCESS. A COMPARATIVE STUDY

Three different methods were used to obtain  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics, i.e. solid-state sintering, mechanical activation (MA) with subsequent thermal treatment, and electrical discharge assisted mechanical milling (EDAMM). The structure and magnetic properties of produced  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  samples were characterized using X-ray diffraction and Mössbauer spectroscopy. The purest  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics was obtained by standard solid-state sintering method. Mechanical milling methods are attractive because the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound may be formed at lower temperature or without subsequent thermal treatment. In the case of EDAMM process also the time of processing is significantly shorter in comparison with solid-state sintering method. As revealed by Mössbauer spectroscopy, at room temperature the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics produced by various methods is in paramagnetic state.

*Keywords:* Aurivillius compound; sintering; mechanical activation; magnetic properties

### 1. Introduction

Ceramics  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  is the first member of the homologous series of Aurivillius compounds  $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$ . These compounds possess layered structure, in which fluorite-like layers  $\{(\text{Bi}_2\text{O}_2)^{2+}\}$  alternate with perovskite-like slabs  $\{(\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+1})^{2-}\}$ , where the number of perovskite-like layers per slab  $m$  may have the values  $3 \leq m \leq 13$  [1]. The orthorhombic unit cell of the Aurivillius  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound contains  $m = 4$  perovskite-like layers. The lattice parameters  $a$  and  $b$  are of the order of 5.4 Å, while the  $c$  parameter is about 41.2 Å. Thermal stability of the Aurivillius compounds decreases with increasing  $m$  number [1]. The first member of family is stable up to about 1020 K when the phase transition from orthorhombic to tetragonal system occurs [2]. At room temperature, the ceramics  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  combines ferroelectric, semiconducting, and antiferromagnetic properties [1-3], which make it very attractive material for applications as sensors, actuators, and digital memory elements [4-6]. Moreover, the Aurivillius  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound offers multiferroic properties, having relatively high magneto-electric coupling coefficient  $\alpha_{ME} \sim 20 \text{ mVcm}^{-1}\text{Oe}^{-1}$  [7] and being one of the few single-phase multiferroics which are in competition for composite materials, e.g. ferroelectric-ferromagnetic composite PZT-ferrite [8].

The well-established technology for production of ceramic materials is solid-state sintering route. Recently,

the series of ceramics  $\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$  was successfully prepared by the authors of the present work using mechanical activation (MA) method with subsequent thermal treatment [9]. The relatively new method, i.e. electrical discharge assisted mechanical milling (EDAMM) [10] may also be used for production of ceramic materials.

In this work, the EDAMM process was applied to obtain  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics for the first time. The structure and magnetic properties of produced  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  samples were characterized using X-ray diffraction (XRD) and Mössbauer spectroscopy (MS). The results of measurements were compared with the data obtained for the analogous samples prepared by solid-state sintering and MA methods. The aim of this study was to determine the effect of the processing conditions on the structure and magnetic properties of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics.

### 2. Experimental details

Three different methods were used to obtain  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics, i.e. solid-state sintering, mechanical activation, and electrical discharge assisted mechanical milling. The appropriate amounts of reagent-grade oxide powders, viz.  $\text{Fe}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{TiO}_2$  (all 99.9 % purity) were thoroughly weighted and mixed according to the reaction:

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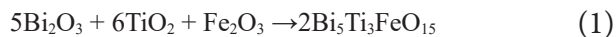
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In the case of solid-state sintering method, the mixture was pressed into compacts, calcined in air at 993 K, re-milled, pressed into discs of 10 mm diameter, and then sintered at various temperatures 1123–1313 K for 2 h [3]. During MA process, firstly the oxides were milled separately in a planetary ball mill Fritsch Pulverisette P5 with stainless-steel balls of 10 mm diameter. The ball-to-powder weight ratio was 10:1, the total mass of the powder was 10 g. The process of milling was conducted in air for 10 h with velocity of 250 rpm. Next, powders were mixed and milled together for 50 h in air. After mechanical activation, isothermal annealing in air at 1073 K was performed in a furnace for 1 h [9]. In the case of EDAMM method, two experiments were performed. In the first experiment,  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  oxides were milled in argon plasma only for 10 min., with vibration amplitude 3 mm of the main stainless-steel electrode powered by AC current. In the second experiment, the EDAMM process was performed on pure Bi, Ti, and Fe metal powders (as starting constituents) in oxygen plasma using stainless-steel electrode covered by protective deposited layer. All starting oxides ( $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ) and metals (Bi, Ti, Fe) used in this work were obtained from Aldrich with minimum 99% purity.

The Philips PW3710-type diffractometer equipped with a Cu lamp was used to perform XRD measurements of all the samples. Detailed phase and structural analyses of diffractograms were performed by Rietveld refinement method based on FullProf software and an X'Pert HighScore Plus computer programme equipped with the newest ICDS and ICDD PDF2 databases.

Room-temperature MS measurements were carried out in standard transmission geometry using a source of  $^{57}\text{Co}$  in a rhodium matrix. All the samples were powders contained inside a self-adhesive transparent foil. The calibration of the spectrometer was performed using a 25  $\mu\text{m}$ -thick metallic iron foil. The values of isomer shift determined from the MS spectra are given in relation to  $\alpha$ -iron.

### 3. Results and discussion

The crystalline structure investigations of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics prepared by sintering and MA methods have been published elsewhere [3, 9]. In the case of the sintering, pure  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  samples were produced during sintering for 2 h at various temperatures in the range of 1123–1313 K. Mechanical activation and isothermal annealing at 1073 K for 1 h produces the Aurivillius  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound with small amount (5 %) of the  $\text{Bi}_{12}\text{TiO}_{20}$  secondary phase. During EDAMM process in the first experiment, the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound was formed after 10 min.; however, only 60 % of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  was obtained and the rest were secondary  $\text{Bi}_{12}\text{TiO}_{20}$  and probably untransformed  $\text{Bi}_2\text{O}_3$  phases. Fig. 1 presents a comparison of XRD patterns for the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics obtained by three different methods. The angular positions of diffraction lines from the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound (Fig. 1a) are the same for all the samples prepared by sintering, MA and EDAMM, respectively.

Some differences may be observed in the intensities of lines for the samples prepared by MA and EDAMM processes (Fig. 1 b and c) in comparison with sintered sample (Fig. 1 a). This effect may be a result of the existence of secondary phases as well as some differences in the preparation process. Numerical fitting of the XRD patterns by the Rietveld method was carried out under an assumption of *Fmm2* (no.42) space group for the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound (PDF2 card no. 01-082-0063, Fig. 1 d). The obtained lattice parameters are as follows:  $a \sim 5.46 \text{ \AA}$ ,  $b \sim 5.44 \text{ \AA}$  and  $c \sim 41.18 \text{ \AA}$  for all the samples. They are in good agreement with the data published by other authors [1, 11].

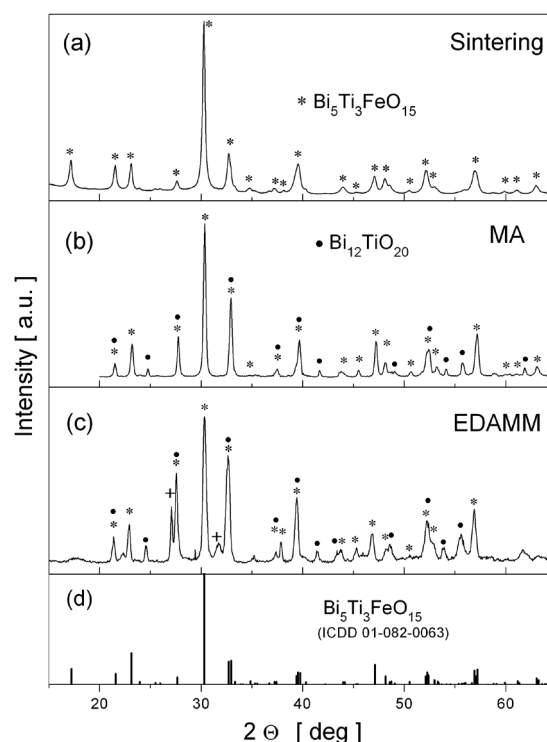


Fig. 1 XRD patterns for the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound prepared by: (a) sintering at 1123 K, (b) MA and annealing at 1073 K, and (c) EDAMM methods. Phase analysis was performed based on the PDF2 card no. 01-082-0063 (d). The peaks from  $\text{Bi}_{12}\text{TiO}_{20}$  are marked according to the card no. 00-034-0097; peaks marked by crosses may come from untransformed  $\text{Bi}_2\text{O}_3$ .

On the basis of XRD results it may be stated that purest ceramics  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  was obtained by standard solid-state sintering method. However, alternative technologies, i.e. mechanical activation and electric discharge assisted mechanical milling have some advantages. In the case of MA method, pure  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound was produced at lower temperature as compared with conventional solid-state sintering technology (lower at least by 50 K). The lowered temperature of thermal treatment might be applied because the mechanical milling, causing large amount of structural defects, enhanced diffusion process. EDAMM process using  $\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  oxides (first experiment) allowed obtaining the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics with significant amount of undesired and un-reacted phases; however, the time of synthesis was much shorter in comparison with sintering and MA methods.



Moreover, additional heat treatment is not required after EDAMM process. Unfortunately, EDAMM of oxides in argon plasma condition, as shown in our experiment, resulted in partial transformation and the method requires further improvement. As mentioned above, the second experiment was carried out using EDAMM, i.e. synthesis of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  from pure Bi, Ti, and Fe metal powders as starting constituents processed in oxygen plasma. It can be assumed that mixture of metals, in stoichiometric amounts, subjected to the EDAMM process in oxygen atmosphere creates the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase. It succeeded partially in our experiment; XRD measurements (pattern is not presented here) confirmed presence of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  phase in about 30%. As previously, the synthesis conditions by EDAMM need further work.

Magnetic property of the studied  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics was determined using Mössbauer spectroscopy. In all cases the measured room-temperature MS spectra revealed double-line pattern which confirms paramagnetic state of the material. As reported earlier by us this ceramics remains paramagnetic down to 2 K [3]. Besides this overall information, Mössbauer spectroscopy provides the knowledge about local magnetic properties, namely the character and values of hyperfine interactions between nuclear probes, i.e.  $^{57}\text{Fe}$  ions and their nearest neighborhood. To accurately characterize the hyperfine interactions, the structural model of the Aurivillius  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound was considered. Fig. 2 presents the elementary cell of the compound together with its projection onto an YZ plane. Note that each perovskite block is offset relative to the next one by  $(a_0/2, b_0/2, c_0/2)$ , where  $a_0$ ,  $b_0$  and  $c_0$  are the lattice parameters of the conventional orthorhombic unit cell. It is known that iron ion may occupy the Ti site, i.e. position in the centre of the oxygen octahedron (B site in perovskite  $\text{ABO}_3$  structure). In the newest theoretical first-principles calculations for the four-layer Aurivillius phase  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  reported in [12], the authors used the 48 atoms unit cell corresponding to the primitive unit cell of the low-symmetry  $A2_{1am}$  structure, which contained eight octahedrally-coordinated B sites (four inner (B1) and four outer (B2) sites, see Fig. 2). In their calculations, ten symmetrically inequivalent configurations were considered, each configuration corresponded to different distribution of Fe and Ti ions over the octahedral B sites. The authors found a slight preference of the  $\text{Fe}^{3+}$  ions to occupy the inner sites which is consistent with recent Mössbauer spectroscopy results reported by Lomanova et al. [13]. As proved by the authors of [13],  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  ions in the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound are distributed over B1 and B2 sites in the ordered manner and the outer B2 sites are preferentially occupied by  $\text{Ti}^{4+}$  ions. The Mössbauer spectra were fitted by two doublets with the following hyperfine interaction parameters: isomer shifts  $\delta_1 = 0.37(2)$  and  $\delta_2 = 0.17(2)$  mm s $^{-1}$  and the quadrupole splittings  $\Delta_1 = 0.60(3)$  and  $\Delta_2 = 0.58(3)$  mm s $^{-1}$  for B1 and B2 sites, respectively [13]. We agree with the statement that since the octahedral surrounding of  $\text{Fe}^{3+}$  ions by oxygen ions over the outer B2 sites of the perovskite-like block is less symmetrical than that over the inner B1 sites; however,  $\Delta_1$  should be lower than  $\Delta_2$ . In the case of isomer shift, both values are characteristic for  $\text{Fe}^{3+}$  ions in the octahedral surrounding; however, such a big difference between the values of  $\delta_1$  and  $\delta_2$  requires significant changes in the nearest neighborhood of  $^{57}\text{Fe}$  ions. As it may be seen in Fig. 2, the iron ions at B1 and B2 sites have six

oxygen ions in the first coordination sphere, next they have eight bismuth ions in the second coordination sphere; so the nearest neighborhood of  $^{57}\text{Fe}$  ions is the same for B1 and B2 sites. The changes may occur in the third coordination sphere where iron and titanium ions are distributed accordingly with the chemical compositions (in the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  compound for one iron ion three titanium ions occur).

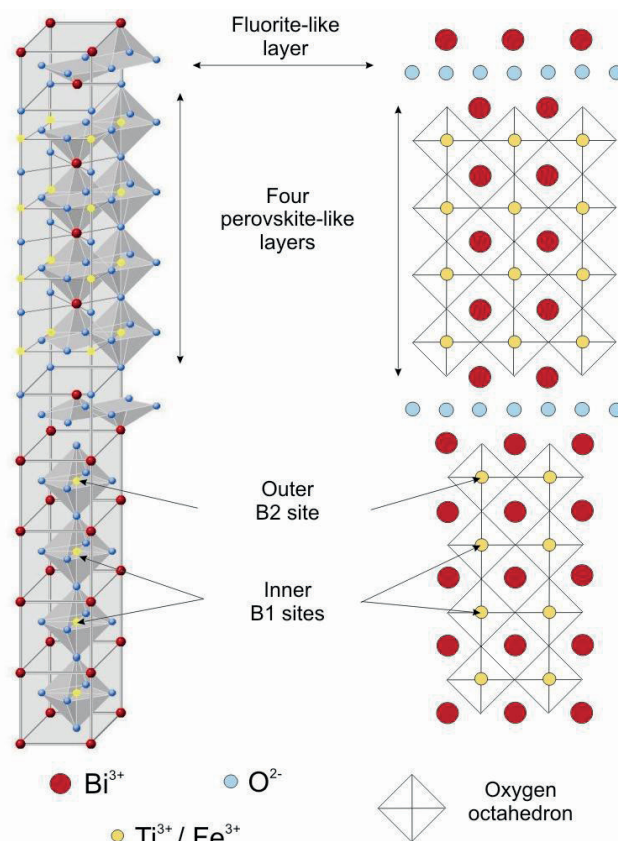


Fig. 2. (a) Unit cell of orthorhombic crystal structure of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics. Four perovskite-like layers  $\{(\text{Bi}_{m+1}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+1})^{2-}\}$  are stacked along [001] direction and separated by fluorite-like layers  $\{(\text{Bi}_2\text{O}_7)^{2-}\}$ . (b) Projection of the unit cell onto an YZ plane. Bi and O atoms are shown as large red and small blue spheres, respectively, whereas the Fe/Ti atoms (yellow spheres) are located inside the octahedra at inner B1 and outer B2 sites

Apart from that ions are distributed randomly or preferentially occupy B1 or B2 sites, we propose the following new interpretation of the results of Mössbauer spectroscopy obtained in the present work. All the MS spectra measured for the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics prepared by three different methods and presented in Fig. 3 were fitted by two doublets with similar values of isomer shifts (reflecting the similar nearest neighborhood of  $^{57}\text{Fe}$ ) and various magnitudes of quadrupole splitting. These two doublets reflect two nonequivalent positions of  $\text{Fe}^{3+}$  ions, i.e. B1 and B2 sites, as described above. The results of numerical fitting are listed in TABLE 1. It may be added that equally good fit of the MS spectra may be achieved when two doublets have the same quadrupole splitting and various isomer shifts (the idea reported by Lomanova et al. [13]). However, an assumption that isomer shifts should be much different at B1 and B2 sites seems to be groundless, since the difference in  $\delta$  value requires a rather big change

TABLE 1

Hyperfine interaction parameters of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics obtained from numerical fitting of the Mössbauer spectra;  $\delta$  – isomer shift relative to  $\alpha$ -iron,  $\Delta$  – quadrupole splitting,  $\Gamma$  – half width at half maximum of spectral lines,  $\chi^2$  – fitting parameter, A – relative area of the component; uncertainty for  $\delta$ ,  $\Delta$  and  $\Gamma$  are given for the last significant numbers in parentheses

Preparation method	$\delta$ [mm s <sup>-1</sup> ]	$\Delta$ [mm s <sup>-1</sup> ]	$\Gamma$ [mm s <sup>-1</sup> ]	$\chi^2$	A [%]	Component
Sintering	0.34(1)	0.47(1)	0.17(1)	1.17	55	Doublet 1, B1 site
1123 K	0.33(1)	0.74(2)	0.17(1)		45	Doublet 2, B2 site
MA 50 h	0.35(1)	0.45(1)	0.17(1)	0.86	54	Doublet 1, B1 site
1073 K	0.35(1)	0.73(2)	0.17(1)		46	Doublet 2, B2 site
EDAMM	0.38(1)	0.55(1)	0.19(1)	0.61	70	Doublet 1, B1 site
oxides, argon plasma	0.36(2)	0.78(2)	0.19(1)		30	Doublet 2, B2 site
EDAMM	0.38(1)	0.48(2)	0.18(1)	0.58	64	Doublet 1, B1 site
metals, oxygen plasma	0.37(2)	0.92(2)	0.18(1)		36	Doublet 2, B2 site

in configuration of valence electrons of  $^{57}\text{Fe}$  probes. This is not expected for iron ions at B1 and B2 sites which have very similar nearest neighborhood.

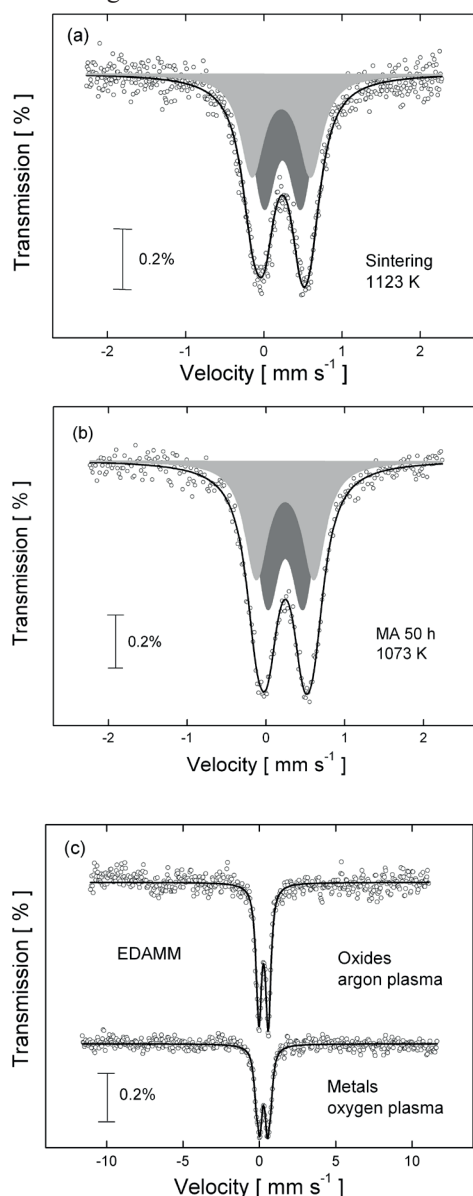


Fig. 3. Fitted room-temperature Mössbauer spectra of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics prepared by (a) solid-state sintering, (b) mechanical

activation (MA) and (c) electrical discharge assisted mechanical milling (EDAMM) from oxides and pure metals. The wider range of velocity in the case of EDAMM shows the absence of magnetic components

Comparing the hyperfine interaction parameters of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics prepared by three different methods, it may be stated that very similar values of isomer shift and quadrupole splitting were obtained for sintered and mechanically activated samples. Also the relative contribution of the doublets to the whole MS spectrum (components are marked in Fig. 3 (a) and (b)) is practically the same for sintering and MA process. For the compounds obtained by EDAMM process, the values of parameters are slightly higher. It may be noted that no magnetically split component was registered in MS spectra (Fig. 3 (c)), it means that the whole amount of iron oxide (in first experiment) and pure iron (in second experiment) used in EDAMM process reacted and formed the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics. Slightly broadened spectral lines in the case of the EDAMM samples may reflect the higher level of internal stress and defects as compared with the compounds prepared by sintering and MA methods.

#### 4. Conclusions

It was shown that the processing conditions of three methods, i.e. solid-state sintering, mechanical activation and electrical discharge assisted mechanical milling have significant effect on the structure and magnetic properties of  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics. The purest samples are produced using standard ceramic technology. Alternative methods, MA and EDAMM, are also attractive considering the temperature of thermal treatment or the time of synthesis; however, the obtained material contains lower or higher level of unwanted phases. Both methods need further works and modifications in order to reduce the secondary phases to a minimum.

Mössbauer spectroscopy contributes significant share to knowledge about magnetic properties of the  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  ceramics. At room temperature, the compounds produced by various methods are in paramagnetic state. Two different positions of iron ions in crystalline lattice may be distinguished, both have non-cubic surroundings, thus the quadrupole splitting of the constituent doublets in Mössbauer

spectra should be different. From a physical point of view the numerical fitting of the spectra with two doublets with similar isomer shifts and different quadrupole splitting is justified.

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